

SOLVENT EXTRACTION AND SEPARATION OF ZINC AND COBALT FROM AMMONIACAL SOLUTION

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ABSTRACT

A process was developed to recover Zn and Co by solvent extraction from the raffinate generated during processing of sea nodules. From a model ammoniacal solution containing 0.2 g/L Zn or 0.2 g/L Co, extraction of Zn and Co by Versatic acid was studied. A maximum of 87% Zn was extracted with 1M Versatic acid in single stage, whereas extraction of Co was negligible due to its higher oxidation state. When Co(III) was reduced to Co(II) by the addition of cobalt powder, 1M Versatic acid extracted 76% Co in a single stage. From the McCabe Thiele diagram number of counter current extraction stages required for complete recovery of Zn and Co from ammoniacal solution was determined. Simulation of counter current extraction of Zn and Co was also carried out. Thus, this process can be used to recover Zn, leaving Co in the raffinate. Then Co can be recovered by solvent extraction with Versatic acid after reducing Co(III) to Co(II) state.

INTRODUCTION

Polymetallic nodules available in the sea bed is being considered worldwide as potential source for valuable metals such as Cu, Ni, Co, Mn, etc. In Indian ocean the reserve of polymetallic nodule is estimated to be 170 billion tonnes containing 0.9-1.1% Cu, 1.0-1.2% ni, 0.1-0.2% Co, 0.08-0.12% Zn, 15-12% Mn, 7-10% Fe etc. At NML a process has been developed to recover Cu and Ni from sea nodules by ammoniacal leaching followed by solvent extraction separation of Cu and Ni from the ammoniacal leach liquor [1]. Raffinate generated in this process contains ~ 0.2 g/L Co and Zn each along with 60 g/L NH₃ and 60 g/L CO₂. Recovery of Co from the raffinate is crucial in view of its short supply and recovery of Zn would be added advantage. Traditionally, Co and Zn from the raffinate are separated by precipitation of Co-Zn cake during ammonia stripping-H₂SO₄/HCl leaching-SX separation of Co and Zn using D2EHPA/Cyanex 272/Aliquat 336 as extractant [2,3]. However, this is a complicated process. Thus it is desired to recover Zn and Co directly from the raffinate and recycle the ammonia solution for leaching purpose of sea nodules.

A number of studies have been reported on the solvent extraction of Zn and Co from ammoniacal solution [4-7]. In the present study, a process has been developed to separate Zn and Co from ammoniacal solution by solvent extraction, thereby simplifying the process flowsheet for extraction and separation of Zn and Co from ammoniacal raffinate eliminating steps like precipitation and acid leaching.

EXPERIMENTAL

Raffinate generated during processing of sea nodules contains ~0.2 g/L Co, Zn, 60 g/L NH₃ and 60 g/L CO₂. Cobalt in the raffinate exists in the Co(III) state. Therefore, model aqueous solutions containing 0.2 g/L Zn or 0.2 g/L Co were prepared by dissolving ZnSO₄ or (Co(NH₃)₆-Cl₃ in 60 g/L NH₃, 60 g/L CO₂ solution and investigated for separation of Zn

and Co by solvent extraction. Organic phases were prepared by dissolving desired amount of Versatic acid in kerosene. Solvent extraction of Zn or Co from ammoniacal solution of above composition was studied by shaking 25 mL each of aqueous and organic phase for 10 min in a separating funnel at room temperature. Preliminary experiments showed that extraction equilibrium was attained within 2 min. Both the phases were then allowed to separate and analysed with the help of Atomic Absorption Spectrometer (ECIL, AAS 4141). Metal content in the aqueous raffinate was determined by AAS, whereas metal content in the organic phase was computed from material balance, however at times organic phase was stripped with dilute sulfuric acid and analysed by AAS to check the material balance. Concentrations of metal ion in the aqueous and organic phases were used to calculate distribution ration (D) and percentage extraction (%E).

RESULTS AND DISCUSSION

Solvent Extraction of Zn from Ammoniacal Solution with Versatic Acid

Extraction of Zn from the ammoniacal solution containing 0.2 g/L Zn, 60 g/L CO₂ and 60 g/L NH₃ was studied using different concentration of Versatic acid in kerosene as diluent, at O/A phase ratio of 1:1. Figure 1 shows that the extraction of Zn increased with increase in concentration of Versatic acid, and a maximum of 87% Zn was extracted with 1M Versatic acid solution. The plot of log *D* versus log [Versatic acid] (Fig. 2) had a slope of 1.85 indicating the involvement of two moles of Versatic acid for the extraction of one mole of Zn from ammoniacal solution. Thus the extraction equilibrium of Zn with Versatic acid (HA) in kerosene can be written as

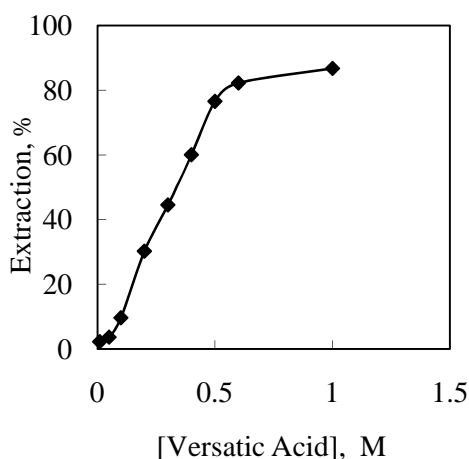
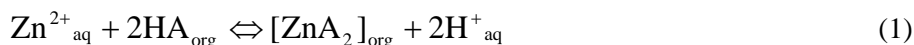


Fig.1 Effect of Versatic acid conc on the extraction of zinc.

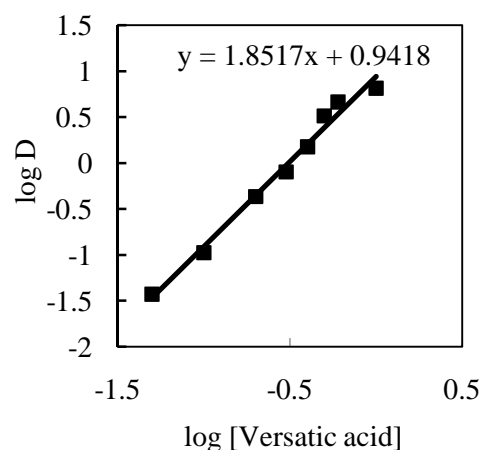


Fig.2 Effect of Versatic acid conc on the distribution ratio of zinc.

The extraction of Zn from ammoniacal solution at different O/A phase ratio was also studied in order to determine the loading capacity of 1M Versatic acid. Figure 3 shows that the percentage extraction of Zn increased from 25% to 98% with the increase in O/A phase ratio from 0.2 to 5. However, loading of Zn in the organic phase increased with the decrease in O/A phase ratio. At the O/A phase ratios 1:3 and 1:5 Zn concentration in the organic phase

was 198.26 ppm, which is also the loading capacity of Versatic acid under the above condition. Number of counter current extraction stages required for complete extraction of Zn from ammoniacal solution was determined from McCabe Thiele diagram. Extraction isotherm for Zn from ammoniacal solution with 1 M Versatic acid is given in Fig.4. The results indicate that a total of three stages are required for complete extraction of Zn from ammoniacal solution containing 0.2 g/L Zn, 60 g/L CO₂ and 60 g/L NH₃ with 1 M Versatic acid in kerosene at O/A phase ratio of 1:1. Simulation of counter current extraction of Zn with 1 M Versatic acid was also carried out for four stages, at the O/A phase ratio of 1:1. The raffinate at each stage was analyzed to understand the transport of metal in the organic phase. At the end of four stages of counter current extraction, 0.198g/L of Zn was loaded into the organic phase. The final raffinate contained 0.003g/L of Zn.

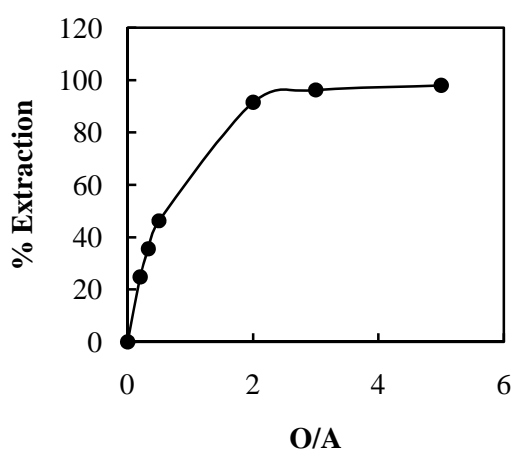


Fig.3 Effect of O/A phase ratio on loading of zinc in the organic phase.

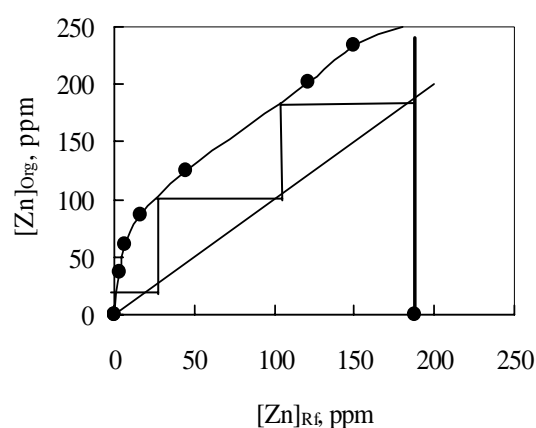


Fig.4 Mc-Cabe Thiele Plot for the extraction of Zinc with Versatic acid.

Solvent Extraction of Co from Ammoniacal Solution with Versatic Acid

As Co(III) from zinc depleted raffinate was not at all extracted with Versatic acid, it was reduced to Co(II) by the addition of a metal with higher oxidation potential. Oxidation potential of Co/Co²⁺ shows that:



cobalt metal can reduce Co(III) rapidly. A 0.1 g cobalt powder was added to 1L of ammoniacal Co(III) solution under nitrogen atmosphere. Within 75 min all the Co(III) were converted into Co(II) state. Potential of the solution also reduced from 201 mV to -29 mV (Fig. 5).

The reduced ammoniacal Co solution containing 0.4 g/L Co, 60 g/L CO₂ and 60 g/L NH₃ was used to study the solvent extraction of Co with Versatic acid solution at O/A phase ratio of 1:1. The extraction of Co increased with increase in Versatic acid concentration. With 1M Versatic acid solution 76% Co was extracted into the organic phase. The plot of Log D vs log [Versatic acid] (Fig. 6) had a slope of 1.5 indicating extraction of CoA₂ species into the organic phase.

Loading capacity of 1 M Versatic acid for Co was determined by varying O/A phase ratio. The extraction of Co increased with increased in O/A phase ratio. At the phase ratio of O/A = 5:1, a maximum of 93% Co was extracted into the organic phase. Figure 6 indicates the loading of Versatic acid at different phase ratio. At phase ratio of O/A = 1:3 and 1:5, 185.92 ppm Co was loaded into the organic phase, which is also the loading capacity of the

1M Versatic acid. Number of counter current extraction stages required for complete extraction of Co from ammoniacal solution was determined from McCabe Thiele plot, it was found that 5 counter extraction stages are required for complete recovery of Co from ammoniacal solution with 1M Versatic acid solution at 1:1 phase ratio. During simulation of counter current extraction 0.19 g/L Co was loaded into the organic phase leaving 0.01 g/L Co in the raffinate.

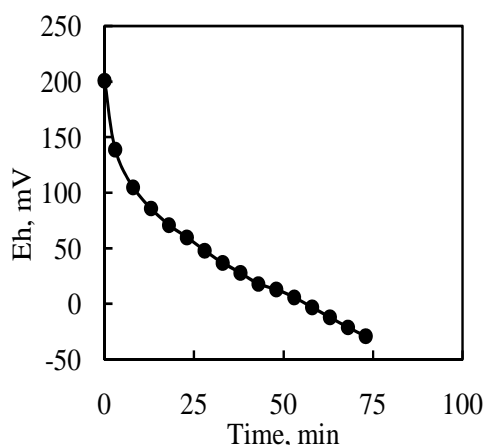


Fig. 5 Change in E_h of cobalt solution with time during reduction of Co(III) to Co(II) in presence of cobalt powder

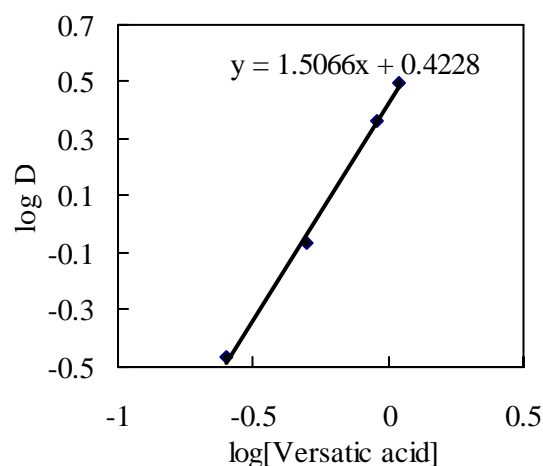


Fig. 6 Effect of Versatic acid conc on the extraction of cobalt from ammoniacal solution

CONCLUSION

Extraction of Zn and Co from model ammoniacal solution similar to the raffinate of sea nodule processing, containing 0.2 g/L Zn or 0.2g/L Co was studied using Versatic acid. With 1M Versatic acid solution Zn was completely recovered in 4 counter extraction stages. However, Co was not at all extracted with Versatic acid because of its higher (+III) oxidation state. After reduction of Co(III) to Co(II) state by the addition of cobalt powder 76% Co was extracted with 1M Versatic acid in a single stage. In 5 counter current extraction stages Co was completely recovered. Thus, Zn from the sea nodule raffinate can be recovered by solvent extraction with Versatic acid, and from the Zn depleted solution Co(III) after reduction to Co(II) can be recovered by solvent extraction with Versatic acid. The ammoniacal solution free of Zn or Co ion can be recycled for leaching purpose. The novelty of the process is that cobalt powder is added to effect reduction of Co(III) and no additional impurity is added which would complicate the separation scheme.

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